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EVIDENCE FOR A STEREOSPECIFIC MICHAELIS-ARBUZOV REARRANGEMENT IN 4-t-BUTYLCYCLOHEXYL DIPHENYLPHOSPHINITE, A CONFORMATIONALLY HOMOGENEOUS SYSTEM[1]—III[2]

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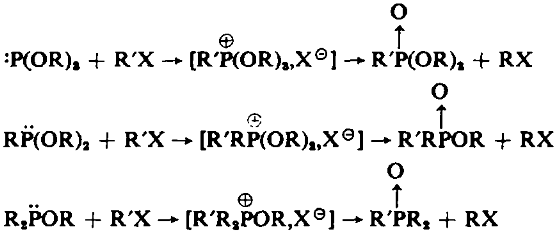
Abstract—Treatment of *trans*-4-butylcyclohexyl diphenylphosphinite with benzyl chloride yielded a mixture containing *cis*-4-butylcyclohexyl chloride. None of the *trans* isomer of the latter halide was detected. Thus support was lent to a stereospecific S_N2 mechanism for the decomposition of quasiphosphonium salts in the second stage of the Michaelis-Arbuzov rearrangement. Further evidence for this mechanism was found in reactions of the *trans*-phosphinite with carbon tetrachloride and with methyl *p*-toluenesulfonate from which only *cis* substituted cyclohexane derivatives were obtained. Structures were established by IR, GLC, TLC and NMR.

INTRODUCTION

Since its discovery in 1898 by Michaelis and Kahn,[6] the Michaelis-Arbuzov rearrangement has proven most valuable in the synthesis of compounds possessing a carbon-phosphorus bond. The accepted mechanism involves two steps: (1) the reaction of a halide with a trivalent phosphorus ester to produce a quasiphosphonium salt, and (2) the subsequent decomposition of this salt to produce a new halide



$$\ddot{P}(OR)_3 + R'X \rightarrow [R'\overset{\oplus}{P}(OR)_3, X^{\ominus}] \rightarrow R'\overset{\overset{O}{\uparrow}}{P}(OR)_2 + RX$$

$$R\ddot{P}(OR)_2 + R'X \rightarrow [R'R\overset{\oplus}{P}(OR)_2, X^{\ominus}] \rightarrow R'R\overset{\overset{O}{\uparrow}}{P}OR + RX$$

$$R_2\ddot{P}OR + R'X \rightarrow [R'R_2\overset{\oplus}{P}OR, X^{\ominus}] \rightarrow R'\overset{\overset{O}{\uparrow}}{P}R_2 + RX$$

and a pentavalent phosphorus compound. This process is illustrated above with the three types of trivalent phosphorus esters in increasing order of reactivity, phosphite < phosphonite < phosphinite.[7] Although an S_N1 type of decomposition for step (2) is

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[1] We gratefully acknowledge the generous support by the Public Health Service, Grant no. GM-10367-04.

[2] For the previous paper in this series, see: K. D. Berlin, C. Hildebrand, A. South, D. M. Hellwege, M. Peterson, E. A. Pier and J. G. Verkade, *Tetrahedron* **20**, 323 (1964).

[3] Predoctoral candidate, 1962–66.

[4] Post-doctorate, 1963–65.

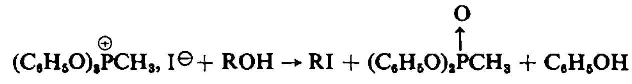
[5] Department of Microbiology.

[6] A. Michaelis and R. Kahn, *Dtsh. Chem. Ges. Ber.* **31**, 1048 (1898).

[7] A. I. Razumov, *J. Gen. Chem. USSR* **29**, 1609 (1959); *Chem. Abstr.* **54**, 8608 (1960).

possible, data available from systems studied to date support an S_N2 process. The most convincing evidence that this decomposition is indeed an S_N2 reaction has been two sterochemical studies.

Landauer and Rydon discovered a novel method[8] of decomposing stable quasi-phosphonium salts. Treatment of triphenoxymethylphosphonium iodide (I) with an

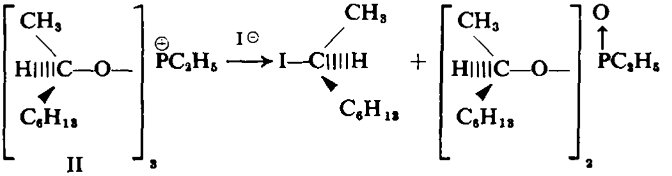


$$(C_6H_5O)_3\overset{\oplus}{P}CH_3, I^{\ominus} + ROH \rightarrow RI + (C_6H_5O)_2\overset{\overset{O}{\uparrow}}{P}CH_3 + C_6H_5OH$$

I

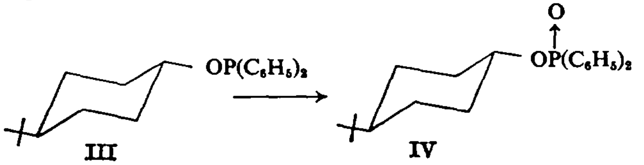
alcohol gave the corresponding alkyl iodide, phenol and the expected phosphonate. By choosing (+)-2-octanol for ROH, they were able to isolate (—)-2-iodoöctane,[9] a result which strongly suggests that an S_N2 mechanism is operative in this reaction. The absence of skeletal rearrangement in reactions in which ROH was neopentyl alcohol, further supports the Walden-type of inversion.

In a classical Michaelis-Arbuzov rearrangement, Gerrard and Green[10] treated tri-2-octyl phosphite, prepared from (+)-2-octanol, with ethyl iodide. Besides the expected phosphonate, they isolated (—)-2-iodooctane, indicating an intermolecular, end-on, three-center dealkylation of tri-2-octyloxyethylphosphonium ion (II) by iodide ion.



II

We have studied the stereochemistry of a classical Michaelis-Arbuzov rearrangement, utilizing the conformationally homogeneous system of *trans*-4-t-butylcyclohexyl diphenylphosphinite (III). The structure of III was confirmed by oxidation in air to the known phosphinate IV.[11]



III IV

Several reviews are available on the scope and mechanism of the Michaelis-Arbuzov rearrangement.[12–14]

RESULTS

A mixture of *cis*- and *trans*-4-t-butylcyclohexanol was used to prepare the *trans*-phosphinite (III) from diphenylphosphinous chloride. The NMR spectrum of the

[8] S. R. Landauer and H. N. Rydon, *Chem. & Ind.* 313 (1951).

[9] S. R. Landauer and H. N. Rydon, *J. Chem. Soc.* 2224 (1953).

[10] W. Gerrard and W. J. Green, *J. Chem. Soc.* 2550 (1951).

[11] K. D. Berlin, T. H. Austin, and M. Nagabhushanam, *J. Org. Chem.* **30**, 1267 (1965).

[12] R. G. Harvey and E. R. De Sombre, *Topics in Phosphorus Chemistry* Vol. 1, p. 57. Interscience New York (1964).

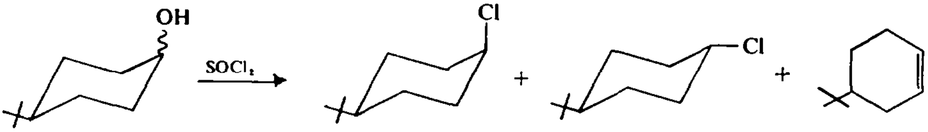
[13] G. M. Kosolapoff, *Organophosphorus Compounds*. Wiley, New York (1950).

[14] G. M. Kosolapoff, *Organic Reactions* Vol. 6, p. 273. Wiley, New York (1951).

redistilled reaction mixture showed three major peaks in the t-butyl region around δ 0·8. The most prominent peak, appearing at 47 c/s downfield from TMS, was assigned to the t-butyl protons in the *trans*-phosphinite (III). A peak appearing at 53·5 c/s, less than one-third the size of that for III, was assigned to the t-butyl protons in the *trans* alcohol. Finally, a third peak in this region at 52 c/s, less than 5% the size of that for III, was assigned to those of *cis*-4-t-butylcyclohexyl diphenylphosphinate (V). These assignments were made by using mixed standard samples. A third and very slow distillation removed the peak at 52 c/s.

Pure *cis*-4-t-butylcyclohexanol (VI) was prepared by column chromatography of the *cis-trans* mixture. Compound VI reacted very slowly with diphenylphosphinous chloride and gave a low yield of *cis*-phosphinate (V); in fact, the largest peak in the t-butyl region of the NMR spectrum of the reaction mixture was assigned to the *cis* alcohol (VI). This absorption was at 55 c/s, and the only other absorption observed in this region was at 52 c/s. The latter absorption was assigned to the t-butyl protons of V and corresponded to the smallest absorption in this region of the spectrum for redistilled *trans*-phosphinite. The oxidation of the *cis*-4-t-butylcyclohexyl diphenylphosphinite to V is apparently very fast at room temperature. A strong P → O band was always visible at 1183 cm^{-1}. Molecular models imply the phosphorus atom in III is somewhat protected. In contrast the *cis* conformer has the phosphorus atom above the ring and readily exposed so facile oxidation is understandable. TLC analysis showed a small amount of diphenylphosphinous chloride in both the *cis*-phosphinate and *trans*-phosphinite preparations.

For the purpose of comparison, authentic samples of *cis*- and *trans*-4-t-butylcyclohexyl chloride (VII and VIII, respectively), were prepared by the method of Greene *et al.*[15] In the last fraction from the distillation of the reaction mixture was obtained the isomeric chlorides, VII and VIII, and a small quantity of 4-t-butylcyclohexene (IX).



cis and *trans* VII VIII IX

The *trans*-phosphinite (III) was stirred in benzyl chloride for two days at room temperature. Addition of petroleum ether precipitated a white solid which was removed by filtration. Although the filtrate was shown by TLC to contain *cis* halide (VII) and olefin (IX), no *trans* halide (VIII) was detected by this method. A spot of much greater intensity was observed for VII in a reaction mixture in which a polar solvent, acetonitrile, had been used. However, again, VIII was absent from the mixture. The white solid contained two major components which could be separated by washing with benzene. The benzene-soluble portion was identified as benzyldiphenylphosphine oxide (X). The benzene-insoluble portion was a high-melting, water-soluble solid. Its water solution gave a white precipitate with silver nitrate. On the basis of these properties, the solid was tentatively identified as a quasiphosphonium salt, *trans*-4-t-butylcyclohexyloxybenzyldiphenylphosphonium chloride (XIa). Its IR spectrum was almost identical to another benzene-insoluble residue (XIb) obtained in

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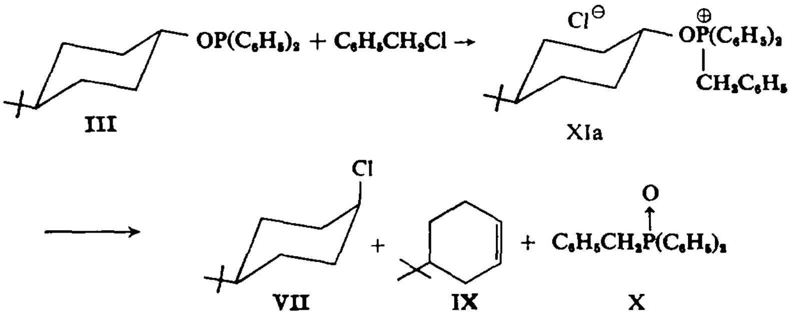
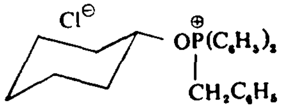
[15] F. D. Greene, C. Chu and J. Walia, *J. Org. Chem.* **29**, 1285 (1964).

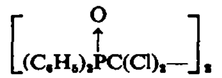




XIb

preliminary experiments by reaction of benzyl chloride with cyclohexyl diphenylphosphinite (Experimental). Thus all the evidence available seems to support structure XIa, although a good elemental analysis was difficult to achieve because of difficulty in removing traces of water. When XIa was heated above its m.p. (290°) for 1 min and immediately allowed to cool to room temperature, olefin IX and a trace of *cis* chloride were detected in the mixture by TLC. Treatment of *trans*-phosphinite (III) with benzyl chloride at high temperature (175°) yielded all of the products found in the room temperature reaction except the *cis*-chloride (VII). The elimination of HCl must accompany the decomposition of the quasiphosphonium salt since the halide VII is unchanged after being heated with phosphinite (III), phosphinate (IV) or phosphine oxide (X).

When III was dissolved in carbon tetrachloride and allowed to stand for ½ hr, a white solid precipitated. After removal of this solid by filtration, *cis*-chloride (VII) was identified in the solution by TLC and NMR. The *trans* isomer (VIII) once again was not detected. The white solid was presumed to be the expected product, diphenyl-(trichloromethyl)-phosphine oxide, but its m.p. of 197–198° did not correspond to the literature value (m.p. reported 138·5—139·5°[16]). Elemental analysis and IR indicated a dimer (XII) of the expected product had been formed, presumably by free-radical coupling.



$$\left[(C_6H_5)_2\overset{\overset{\displaystyle O}{\uparrow}}{P}C(Cl)_2-\right]_2$$

XII

Myers *et al.*[17] discovered that phosphonate esters could be prepared from phosphites utilizing alcohols in the form of their sulfonate esters instead of the more difficultly accessible halides. Denney and Giacin[18] studied this reaction in detail with methyl

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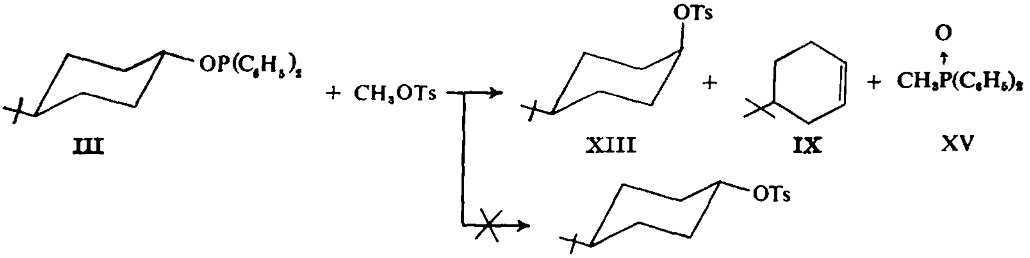
[16] F. M. Kharrasova and G. Kamai, *Zh. Obshch. Khim.* **34**, 2195 (1964); *Chem. Abstr.* **61**, 10705 (1964).

[17] T. C. Myers, S. Preis and E. V. Jensen, *J. Amer. Chem. Soc.* **76**, 4172 (1954).

[18] D. B. Denney and J. Giacin, *Tetrahedron Letters* 1747 (1964).

p-toluenesulfonate and demonstrated its similarity to the Michaelis-Arbuzov rearrangement with respect to the quasiphosphonium intermediates involved. In preliminary experiments we were able to obtain methyldiphenylphosphine oxide and cyclohexyl *p*-toluenesulfonate from a reaction of methyl *p*-toluenesulfonate with cyclohexyl diphenylphosphinite. Because of the success of these experiments, it was decided to determine if conversion of *trans*-4-t-butylcyclohexyl diphenylphosphinite (III) to *cis*-4-t-butylcyclohexyl *p*-toluenesulfonate (XIII) was stereospecific. Samples of the



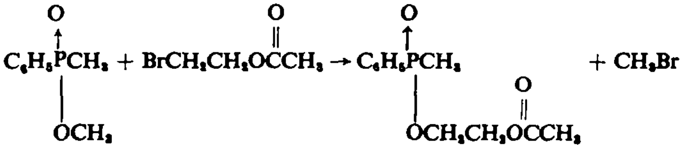
III XIII IX XV

XIV

cis tosylate (XIII) and its *trans* isomer (XIV) were prepared by well-established procedures[19,20] from the isomeric alcohols and *p*-toluenesulfonyl chloride.

The *trans*-phosphinite behaved in the expected manner, producing the ester (XIII) upon reaction with methyl tosylate at 135°. Identification of XIII in the reaction mixture by TLC was inconclusive because of a large excess of methyl tosylate, which had nearly the same R_f value as XIII, thereby obscuring it. However, GLC separated the two esters cleanly, and the *cis*-sulfonate ester (XIII) was shown to be in both the known and the reaction mixture by applying mixed injections. TLC was used successfully to detect olefin IX and methyldiphenylphosphine oxide (XV) and to confirm the absence of *trans*-tosylate (XIV).

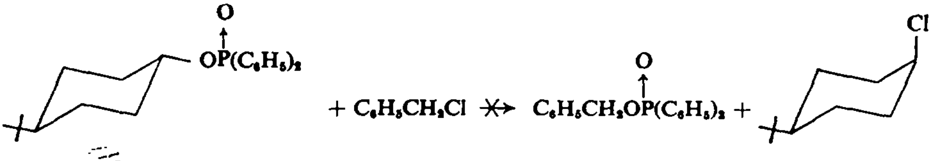
Harwood and Grisley[21] have shown that reactive halides will sometimes produce Michaelis-Arbuzov products with phosphinates (XVI + XVII → XVIII).



$$C_6H_5\underset{\underset{OCH_3}{|}}{\overset{\overset{O}{\uparrow}}{P}}CH_3 + BrCH_2CH_2O\overset{\overset{O}{\|}}{C}CH_3 \rightarrow C_6H_5\underset{\underset{OCH_2CH_2O\overset{\overset{O}{\|}}{C}CH_3}{|}}{\overset{\overset{O}{\uparrow}}{P}}CH_3 + CH_3Br$$

XVI XVII XVIII

Since a trace of *trans*-phosphinate (IV) was detected by TLC in the *trans*-phosphinite (III) an attempt was made to determine if an authentic sample of IV would react with



IV XIX VII

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[19] R. S. Tipson, *J. Org. Chem.* **9**, 235 (1944).

[20] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.* **77**, 5562 (1955).

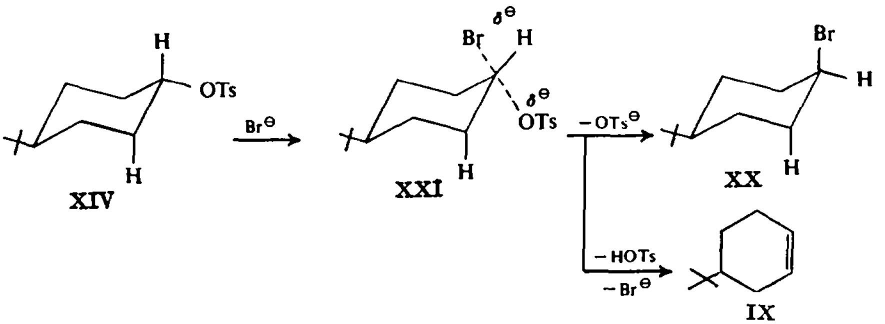
[21] H. J. Harwood and D. W. Grisley, Jr., *J. Amer. Chem. Soc.* **82**, 423 (1960).

benzyl chloride to produce benzyl diphenylphosphinate (XIX). Neither XIX nor the expected chloride (VII) were found by TLC after the phosphinate (IV) and benzyl chloride were stirred together at room temperature for two days. Evidence from the literature[21,22] seems to indicate that elevated temperatures are required for this type of reaction.

DISCUSSION

Because the t-butyl group is so bulky, cyclohexyl compounds having this group attached to the ring consist almost entirely of molecules in a conformation in which t-butyl is in an equatorial position. Thus the 4-t-butylcyclohexyl group is made conformationally homogeneous by a remote but compelling force, and the system appears to be ideal for stereochemical studies of the type discussed herein. Studies of nucleophilic substitution at the C-1 atom of this group have already proven to be of significant value in differentiating between the classical S_N1, S_N2, and S_Ni mechanisms.[23]

Winstein *et al.*[24] have investigated the bimolecular substitution of tosylate ion by bromide ion in this same conformationally rigid system.



Reaction of *trans*-tosylate (XIV) with lithium bromide yielded only the *cis* isomer of 4-t-butylcyclohexyl bromide XX, indicating that an S_N2 conversion had indeed occurred. The appearance of olefin IX in the product was explained in terms of an actual intermediate XXI, electronically and geometrically similar to the transition state in a classical S_N2 displacement. It was proposed that a non-stereospecific elimination was competing with the substitution reaction, the former proceeding by a process which disengaged both nucleophiles, ^{-}OTs and Br^{-}, along with a β-proton.

Whether or not the production of IX is accomplished in this fashion, the analogy between this reaction and the three examples discussed in this paper seems evident. The first example (A) supports the evidence obtained by Gerrard and Green[10] for an S_N2 mechanism in the second step of the classical Michaelis-Arbuzov rearrangement.

The second example (B) may follow a radical-chain course, as evidenced by the dimerized product (XII) and the brief induction period. The stereospecificity in this case might again be attributed to S_N2 displacement on a quasiphosphonium salt.

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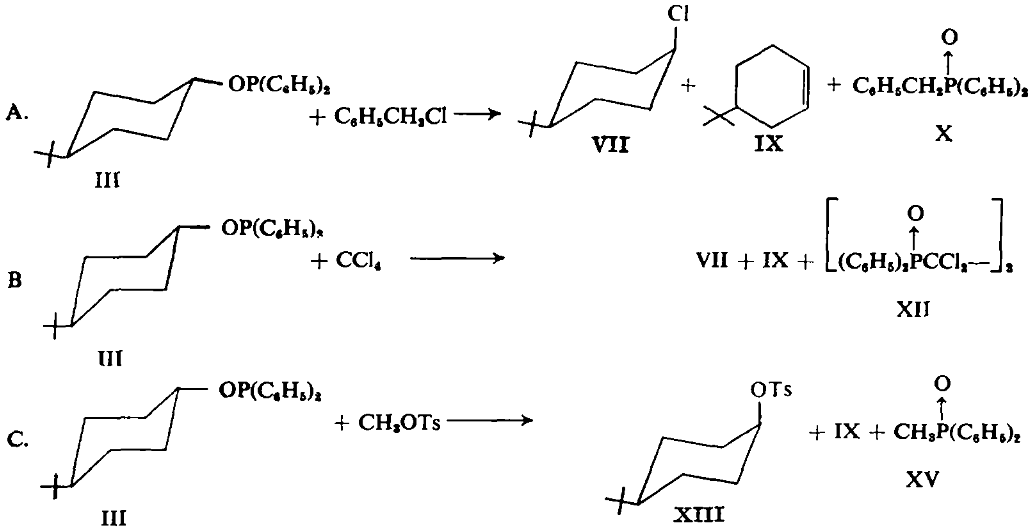
[22] B. A. Arbuzov *et al.*, *Khim. i Primenenie Fosfororgan. Soedienii, Akad. Nauk S.S.S.R., Trudy* 1-oĭ *Konferents.*, 62 (1955); *Chem. Abstr.* 52, 239 (1958).

[23] E. L. Eliel, *Stereochemistry of Carbon Compounds* Ch. 8. McGraw-Hill, New York (1962); E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* Ch. 2. Interscience, New York, N.Y. (1965), and Refs. cited therein.

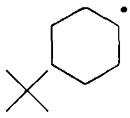
[24] S. Winstein, D. Darwish and N. J. Holness, *J. Amer. Chem. Soc.* 78, 2915 (1956).



Although no such salt has been isolated, a reasonable mechanism can be postulated involving this intermediate. Cadogan[25] has proposed such a mechanism, based on the absence of rearrangement, dimerization, or disproportionation products characteristic of ·R radicals in his products. In a study of the decomposition of alkyl hypochlorites,

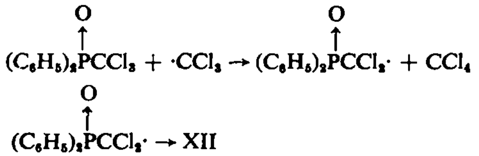
$$RO_3P\colon + \cdot CCl_3 \rightarrow (RO)_3\dot{P}CCl_3 \xrightarrow{CCl_4} (RO)_3\overset{\oplus}{P}CCl_3,\overset{\ominus}{Cl}$$

Greene[15] showed that the 4-t-butylcyclohexyl radical (XXII) can extract a chlorine atom from a suitable source to give *both* isomers of 4-t-butylcyclohexyl chloride (VII and VIII) in a ratio *cis*:*trans* = 2:1. Consequently in the reaction of III with carbon



XXII

tetrachloride, XXII appears to be an improbable intermediate, and the quasiphosphonium salt is favored. Formation of XII might be envisioned as occurring in a manner analogous to the reaction of bromotrichloromethane with triethyl phosphite.[26]



$$(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}CCl_3 + \cdot CCl_3 \rightarrow (C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}CCl_2\cdot + CCl_4$$

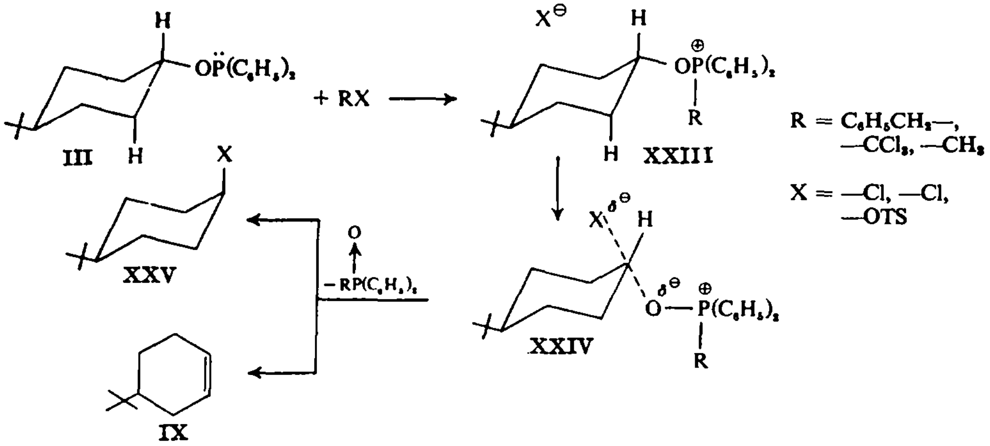
$$(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}CCl_2\cdot \rightarrow XII$$

[25] J. I. G. Cadogan and W. R. Foster, *J. Chem. Soc.* 3071 (1961).

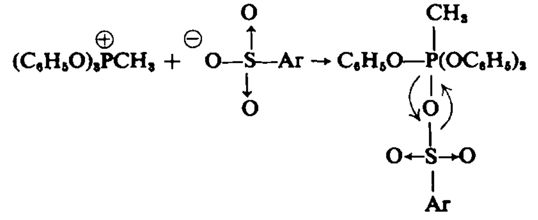
[26] P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.* 2953 (1963). These workers did not find a coupling product although the high boiling fraction was not completely analyzed. An analogous radical, $(RO)_2P(O)CCl_2\cdot$, was shown to react with more phosphite to give $(RO)_2P(O)CCl_2P(O)(OR)_2$. The coupling of $(C_6H_5)_2P(O)CCl_2\cdot$ in our system may occur since attack on the phosphinite (III) appears difficult because of steric hindrance. Radical intermediates in the reaction of bromoform with triphenylphosphine have been suggested; see F. Ramirez and N. McKelvie, *J. Amer. Chem. Soc.* **79**, 5829 (1957).

The third example (C) illustrates the effectiveness of compounds possessing a phosphoryl (P → O) function as leaving groups, placing them ahead of the tosylate anion in order of increasing facility of departure. Moreover, it appears to be the first attempt to demonstrate that rearrangements of trivalent phosphorus esters by tosylates proceed by an S_N2 mechanism as do the analogous reactions with halides.

All three examples could conceivably proceed by the same course as that proposed by Winstein[23] for substitution of tosylate by bromide in this related system. The quasiphosphonium salt (XXIII) might exist as shown, as an ion-pair, or as a pentacovalent



compound. The latter form has been suggested by Denney,[18] the intermediate (XXVI) in his system decomposing as shown. This mechanism is unlikely in the present system XXIII because it should result in retention of configuration. The most logical mechanistic approach to this problem appears to stem from the ionized salt (XXIII),



$$(C_6H_5O)_3\overset{\oplus}{P}CH_3 + \overset{\ominus}{O}-\underset{\downarrow O}{\overset{O \uparrow}{S}}-Ar \rightarrow C_6H_5O-\underset{O-\underset{Ar}{\overset{}{S}}(\rightarrow O)(\leftarrow O)}{\overset{CH_3}{P}}(OC_6H_5)_3$$

XXVI

yielding the "intermediate" XXIV, which is similar to the transition state which best explains the decomposition of quasiphosphonium salts in many Michaelis-Arbuzov rearrangements.[12] Compound XXIV could undergo "merged substitution and elimination" by the same route as that proposed for XXI,[28] producing XXV, IX and phosphine oxide. The analogy seems justified in view of the similarity of the systems and products observed. In any case there is stereospecificity in the Michaelis-Arbuzov rearrangement involving III with benzyl chloride, carbon tetrachloride and methyl tosylate.

EXPERIMENTAL[27]

Cyclohexyl diphenylphosphinite. To a solution of cyclohexanol (25 g, 0·25 mole) and excess Et_3N in 200 ml benzene was added dropwise a solution of diphenylphosphinous chloride (55 g, 0·25 mole) in 50 ml of benzene with stirring under N_2. The addition was performed over 40 min to avoid heating the mixture above 45°, and the mixture was stirred for 4 hr at room temp, followed by heating at reflux for 2 hr. The mixture was then cooled and filtered under N_2 to remove the amine hydrochloride. Removal of solvent gave an oil which was distilled, b.p. 160–162° (0·3 mm); yield, 56·5 g; ν_{max}^{film} (cm^{-1}): 1440 ($P–C_6H_5$), 1047, 1036, 980; NMR (δ values): 1·02–2·20 (multiplet, cyclohexyl protons), 7·2–8·3 (multiplet, aryl protons). (Found: C, 75·89; H, 7·19; P, 11·04; Calc. for $C_{18}H_{21}PO$: C, 76·05; H, 7·39; P, 10·92%.)

trans-4-t-*Butylcyclohexyl diphenylphosphinite* (III). This compound was prepared employing essentially the same conditions as those of the previous experiment. Thus from a mixture of 39·0 g. (0·250 mole) 4-t-butylcyclohexanol,[28] 25·2 g (0·250 mole) Et_3N, 55·1 g (0·250 mole) diphenyl-phosphinous chloride, and 300 ml benzene there was obtained 30·5 g III, b.p. 174–184° (0·1 mm) which solidified upon standing, m.p. 30–55°. Subsequent distillations gave material of higher purity, b.p. 175–178° (0·1 mm), as evidenced by NMR (see Results). ν_{max}^{film} (cm^{-1}): 1434 ($P–C_6H_5$), 984 (P—O—C), 738 and 695 (C_6H_5—); NMR (δ values, C_6H_6 with TMS): 0·77 (singlet, t-butyl), 3·9 (broad multiplet, axial[29] tertiary proton), "methylene envelope".[30] (Found: C, 78·26; H, 8·72; P, 8·90; Calc. for $C_{22}H_{29}OP$: C, 77·62; H, 8·59; P, 9·10%.)

cis-4-*t-Butylcyclohexanol* (VI). This sample was prepared in a manner similar to Winstein's method.[30] A sample of 4-t-butylcyclohexanol[28] (7·5 g) was chromatographed through 250 g of acid-washed alumina, using light pet. ether (b.p. 30–60°) as the eluant. The first fraction had a m.p. of 49·50° and appeared to be 4-t-butylcyclohexanone (reported m.p. 49–50°[31]). The second fraction (0·4 g) consisted of material which melted at 81–82°, almost 100% *cis*-alcohol. Only one peak for tertiary hydrogen appeared in the NMR spectrum at δ 4·10. The half-width was ca. 8–10 c/s, indicating an equatorial proton.[29]

cis-4-*t-Butylcyclohexyl diphenylphosphinate* (V). A solution of 0·22 g (0·001 mole) diphenylphosphinous chloride in 4 ml of benzene was added to a solution of 0·16 g (0·001 mole) VI and 0·10 g (0·001 mole) Et_3N amine in 8 ml benzene. This preparation differed from that of III as follows: the addition was accomplished in 1 min with less than 10° rise in temp and much less precipitation of amine hydrochloride. The phosphinate was separated by TLC: ν_{max}^{film} (cm^{-1}): 1433 ($P–C_6H_5$), 1193 ($P\rightarrow O$), 958 (P—O—C), 741 and 693 (C_6H_5—); NMR (δ values, C_6H_6 with TMS): 4·20 and 3·93 (multiplets, equatorial[28] tertiary protons), "methylene envelope",[30] two t-butyl peaks (see Results).

cis- *and* trans-4-*t-Butylcyclohexyl chlorides* (VII *and* VIII). The methyl used here was essentially that of Greene *et al.*,[16] except that only a simple distillation was performed, which yielded 3 fractions. The first, b.p. 32–40° (0·6 mm), was mostly IX (R_f = 0·77); and the third, b.p. 53–58° (0·4 mm), was a mixture of VII and VIII containing a trace of IX. TLC gave R_f values of 0·32, 0·47 and 0·77 respectively. A portion of the latter mixture (4·3 g; ca. 0·025 mole) was treated with 4·0 g (0·7 mole) KOH in 20 ml of 95% EtOH under a gentle reflux for 1 day. Distilled water was added, and this mixture was extracted twice with pet. ether. The ether layers were combined, dried ($MgSO_4$), and evaporated to an oily, clear liquid identified by TLC as a mixture of VIII and IX (R_f values 0·47 and 0·77, respectively).

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[27] All m.ps are corrected; all b.ps are uncorrected. The elemental analyses were performed by Galbraith Laboratories. The IR spectra were obtained on a Beckman IR-5A instrument as films on NaCl cells or as KBr pellets. All NMR spectra were recorded by a Varian A-60 instrument. Unless otherwise stated, the solvent employed was CCl_4 containing tetramethylsilane as an internal standard. GLC analyses were performed using an Aerograph Hy-Fi A-550 (hydrogen flame ionization detector) instrument. TLC analyses were performed using 5 mm × 20 mm glass plates spread with a 250 μ layer of activated silica gel. The plates were eluted with carbon tetrachloride containing a trace of acetone, and they were developed in iodine vapor.

[28] Columbia Organic Chemicals, Columbia, South Carolina, m.p. 66–68°, containing approximately 65% *trans* isomer.

[29] Half-widths of less than 12 c/s are characteristic of equatorial protons; see A. Hassner and C. Heathcock, *J. Org. Chem.* **30**, 1748 (1965), and Refs. cited therein.

[30] This absorption, generally extending from about δ 0·7 to 2·7, is characteristic of the methylene protons in the rigid cyclohexyl ring in this system.

[31] L. Schmerling, *J. Amer. Chem. Soc.* **69**, 1121 (1947).

An IR spectrum of the VII–VIII mixture supported the structures proposed and compared favorably with the spectra of the individual compounds published by Greene.[15] The peaks for axial (693 cm^{-1}) and equatorial (726 cm^{-1}) chlorine were observed. An NMR spectrum showed a multiplet centered around δ 4·30; after treatment with ethanolic KOH, this peak had disappeared and olefinic protons for IX were clearly visible at δ 5·58, along with a broad multiplet centered at δ 3·67. This is in accord with the results reported by Greene[15] for VII and VIII.

Reaction of cyclohexyl diphenylphosphinite with benzyl chloride. A mixture of 5·78 g (0·02 mole) cyclohexyl diphenylphosphinite and 11·12 g (0·08 mole) benzyl chloride was heated under N_2 over boiling *o*-dichlorobenzene at 180° for 26 hr. From the solids which settled out upon cooling were obtained two compounds, benzene-soluble and benzene-insoluble. The benzene-soluble material was identified as X. The benzene-insoluble material was tentatively identified as XIb, m.p. 267–268°; ν_{max}^{KBr} (cm^{-1}): 1439 (P–C_6H_5), 1158, 1114, 868, 797, 751, 698.

From the mother liquors, benzyl chloride and chlorocyclohexane were identified by GLC, using a 6′ × ⅛″ column packed with 5% Silicone 30 on acid washed Chromosorb G. Retention times at 110°: chlorocyclohexane, 1·5 min; benzyl chloride, 3·5 min.

Reaction of III *with benzyl chloride.* A mixture of 3·0 g (0·0088 mole) of III and 1·3 g (0·010 mole) benzyl chloride was stirred under N_2 for 2 days. Pet. ether was added until precipitation occurred.

TLC of the filtrate showed the presence of VII and IX but not VIII.

The white solid was washed several times with benzene. The benzene washings were combined, and pet. ether was added until precipitation occurred. A white solid (2·5 g) collected melted at 193–194° and was identified as X by IR, NMR, and a mixture m.p. determination.

The benzene-insoluble portion of the original white solid was recrystallized from water. Large white crystals were obtained, m.p. 268–270° with dec. A drop of $AgNO_3$ solution was added to a few drops of an aqueous solution of this material, which then formed a white precipitate that darkened upon exposure to light. The material was assigned a quasiphosphonium salt structure (XIa), ν_{max}^{KBr} (cm^{-1}): 1432 (P–C_6H_5), 1152, 1113, 867, 797, 751, 698. (Found: C, 73·91; H, 6·16; Cl, 8·43; P, 7·45; Calc. for $C_{29}H_{36}ClOP$: C, 74·58; H, 7·77; Cl. 7·59; P, 6·63%.)

The effect of a polar solvent on the rearrangement was demonstrated by dissolving the phosphinite (amounts of reactants were as before) in a minimum of acetonitrile before adding benzyl chloride. TLC showed the *cis*-chloride to be present in higher concentration in the product. The effect of higher temps was demonstrated by heating a mixture of III and benzyl chloride at 175° over boiling *o*-dichlorobenzene for 150 hr. TLC showed no *cis*-chloride in the product of this reaction. Thermal decomposition of 0·3 g (0·64 mmole) of the benzene-insoluble XIa at 290° for 1 min gave a product which showed only a trace of *cis*-chloride *via* TLC. Longer reaction times yielded only olefin; however, an attempt to dehydrochlorinate the *cis*-chloride in the presence of XIa was unsuccessful. Similarly, all attempts to dehydrochlorinate either the *cis*- or *trans*-chloride in the presence of X, III, or IV, were unsuccessful.

Reaction of III *with carbon tetrachloride.* A sample of III (2·5 g, 0·074 mole) was dissolved in 3·9 ml (6·2 g, 0·04 mole) CCl_4. After a brief induction period, the reaction vessel began to feel warm, and white crystals began to form in the solution. After about ½ hr, these crystals were recovered by filtration and recrystallized, first from CH_2Cl_2–pet. ether and then from MeOH, 0·15 g, m.p. 197–198°; ν_{max}^{KBr} (cm^{-1}): 1440 ($P \rightarrow C_6H_5$), 1200 ($P \rightarrow O$), 748, 725, 697. (Found: C, 54·45; H, 3·86; Cl, 24·66; P, 10·64; Calc. for $C_{26}H_{20}Cl_4O_2P_2$: C, 54·96; H, 3·55; Cl, 24·96; P, 10·90%.) A dimeric structure (XII) was assigned to the solid. The only other product isolated was IV. The *cis*-chloride (VII) and IX were detected in the filtrate by TLC in the usual manner. When the reaction was carried out in an NMR tube with TMS, a peak appeared at δ 4·48 with a half-width of ca. 10 c/s. This absorption was assigned to the equatorial[29] tertiary proton at C-1 in VII. No trace of a signal around δ 3·7 was observed for tertiary axial hydrogen at C-1, and thus VIII appeared to be absent. A peak at δ 5·78 was assigned to vinyl protons in IX.

Cyclohexyl p-*toluenesulfonate.* This ester was prepared by the method of Tipson,[18] ν_{max}^{film} (cm^{-1}): 1362 and 1180 (sulfonate ester), 939 (S—O—C), 816 (*p*-disubstituted phenyl). NMR (δ values): 1·5 (broad multiplet, methylene protons), 2·42 (singlet, methyl protons), 4·5 (broad multiplet, tertiary proton), 7·55 (A_2B_2 quartet, J_{AB} = 8 c/s, δ_ν = 26 c/s, aryl protons); relative intensities 11:3:1:4.

trans-*4-t-Butylcyclohexyl* p-*toluenesulfonate* (XIV). This ester was prepared in a similar fashion as described for cyclohexyl *p*-toluenesulfonate. Thus a mixture of 15·6 g (0·100 mole) of 4-*t*-butylcyclohexanol[28] and 21·0 g (0·110 mole) *p*-toluenesulfonyl chloride in 100 ml of pyridine yielded 22·9 g

(76·3% yield) crude material. Recrystallization from pet. ether containing a trace of AcOEt yielded white crystals, m.p. 87–89° (m.p. pure *trans* isomer = 89·4–90°[30]); ν_{max}^{KBr} (cm^{-1}): 1348 and 1180 (sulfonate ester), 952 (S—O—C), 820 (*p*-disubstituted phenyl). NMR (δ values): "methylene envelope",[30] 0·80 (singlet, t-butyl protons), 2·42 (singlet, methyl protons), 4·25 (broad mutliplet, tertiary axial[29] proton at C-1), 7·48 (A_2B_2 quartet, JAB = 8 c/s δ_ν = 26 c/s aryl protons); relative intensities 18 (methylene + t-butyl): 3:1:4.

cis-4-*t-Butylcyclohexyl* p-*toluenesulfonate* (XIII). This ester was prepared by the method of Winstein,[19] m.p. 79–80°; ν_{max}^{KBr} (cm^{-1}): 1348 and 1171 (sulfonate ester), 914 (S—O—C), 815 (*p*-disubstituted phenyl).

Reaction of cyclohexyl diphenylphosphinite with methyl p-*toluenesulfonate.* A mixture of 2·9 g (0·01 mole) cyclohexyl diphenylphosphinite and 1·9 g (0·01 mole) methyl *p*-toluenesulfonate was heated in a tube under N_2 over boiling xylene (at approximately 135°) for 72 hr. TLC examination, using mixed standard samples, showed cyclohexyl *p*-toluenesulfonate (R_f = 0·50) and XV (R_f = 0·10) to be the major products.

Reaction of III *with methyl* p-*toluenesulfonate.* A mixture of 3·4 g (0·01 mole) III and 1·9 g (0·01 mole) *p*-toluenesulfonate was heated under N_2 over boiling zylene (135°) for 17 hr, during which time the mixture separated into 2 layers. As the mixture cooled, the bottom layer turned to a semi-solid. The top layer was removed and was found to consist chiefly of IX from its IR spectrum. Phosphine oxide (XV) and methyl tosylate were identified in the bottom layer *via* TLC, and XIV was shown to be absent. The spot for *cis*-tosylate was obscured by methyl tosylate, so XIII was identified by GLC, using a 6′ × ⅛″ column packed with 5% Silicone 30 on 80/100 mesh, acid-washed, DMCS-treated Chromosorb G. Retention times at 145°: *cis*-tosylate (XIII), 2 min; methyl tosylate, 12 min.